(54) Title: MITIGATION OF RADIATION INDUCED SURFACE CONTAMINATION

(57) Abstract: A process for mitigating or eliminating contamination and/or degradation of surfaces having common, adventitious atmospheric contaminants adsorbed thereon and exposed to radiation. A gas or a mixture of gases is introduced into the environment of a surface(s) to be protected. The choice of the gaseous species to be introduced (typically a hydrocarbon gas, water vapor, or oxygen or mixtures thereof) is dependent upon the contaminant as well as the ability of the gaseous species to bind to the surface to be protected. When the surface and associated bound species are exposed to radiation reactive species are formed that react with surface contaminants such as carbon or oxide films to form volatile products (e.g., CO, CO_2) which desorb from the surface.

MITIGATION OF RADIATION INDUCED SURFACE CONTAMINATION

BACKGROUND OF THE INVENTION

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The present invention is directed generally to a process for mitigating degradation and contamination of surfaces caused by radiation induced breakdown of molecules and their subsequent reaction and/or deposition on these surfaces. More particularly, the process disclosed herein is directed to

10   protection of the surfaces of components of a lithographic stepper, such as the mask and imaging optics, from the consequences of radiation induced molecular breakdown.

Photolithography is a well-known technique for applying patterns to the surface of a workpiece, such as a circuit pattern to a semiconductor chip or

15   wafer. This technique has the advantage of being able to faithfully reproduce small and intricate patterns. Traditional photolithography involves applying electromagnetic radiation to a mask having openings formed therein (transmission mask) such that the light or radiation that passes through the openings is applied to a region on the surface of the workpiece that is coated

20   with a radiation-sensitive substance, e.g., a photoresist. The mask pattern is reproduced on the surface of the workpiece by removing the exposed or unexposed photoresist. However, the capabilities of conventional photolithographic techniques have been severely challenged by the need for circuitry of increasing density and higher resolution features. The demand for

25   smaller feature sizes has inexorably driven the wavelength of radiation needed to produce the desired pattern to ever-shorter wavelengths. As the wavelength of the applied radiation is made shorter the energy of the radiation becomes greater to the point where the radiation can cause the decomposition of

molecules adsorbed on or proximate to a surface to produce reactive species that can attack, degrade, or otherwise contaminate the surface.

While short wavelength radiation can directly dissociate molecules, secondary electrons, created by the interaction of this radiation with surfaces,

5   are the primary agents for molecular dissociation. Low energy (5-10 eV) secondary electrons are known to be very active in breaking chemical bonds by direct ionization of adsorbed molecules or by electron attachment, wherein a secondary electron binds to a molecule producing a reactive negative ion that then de-excites to a dissociated product. Any type of radiation (photons,

10   electrons, ions, and particles) that is energetic enough to liberate electrons can create secondary electrons; typically, energies of about 4-5 eV are required. Consequently, radiation induced contamination, i.e., contamination of surfaces by reactive species produced by secondary electrons originating from radiative interactions, will most certainly occur in lithographic processes that use

15   energetic radiation such as: extreme ultraviolet lithography (photon energy of about 100eV), projection electron lithography (electron energy of about 50-100 keV), ion beam lithography (ion energy >10keV), 193 nm lithography (photon energy of about 6.4 eV) and 157 nm lithography (photon energy of about 7.9 eV). Thus, the potential for contamination of critical lithographic components,

20   such as masks and optical surfaces, and degradation of their operational capability is present in all the advanced lithographic processes.

A mechanism for the contamination of surfaces having gaseous species adsorbed thereon and exposed to an incident flux of radiation is illustrated schematically in Fig. 1. Here, surface 110 has both hydrocarbon and water

25   molecules adsorbed thereon. The term "hydrocarbon" can include any carbon containing species. Exposure to a radiation flux causes secondary electrons to be emitted from surface 110 that can dissociate the adsorbed hydrocarbon molecules to form reactive carbon fragments that can form a graphite layer on

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the surface. By way of example, exposure of a Si-terminated Mo/Si multilayer mirror to a flux density of about 330 mW/mm^2 of 13.4 nm radiation at a background pressure of 1x10^{-7} Torr for about 45 hours results in the growth of a layer of graphitic carbon having a thickness of about 230 Å. The graphitic

5   carbon film, produced by the secondary-electron-induced dissociation of hydrocarbon molecules adsorbed on the surface from this environment reduced mirror reflectivity from 66% to 12%, a loss in reflectivity that would render the multilayer mirror inoperable in a lithographic stepper.

Similarly, secondary electrons emitted from surface 110 in response to

10   the radiation flux can dissociate adsorbed water molecules to form reactive oxygen species that can oxidize a surface to form an oxide film that can degrade the reflectivity of a mirror by absorption of radiation. Thus, oxidation resulting from radiation induced dissociation of water molecules can catastrophically and irreversibly damage optical surfaces. By way of example, exposure of a Si-

15   terminated Mo/Si multilayer mirror to a flux density of about 330 mW/mm^2 of 13.4 nm radiation and 1x10^{-7} Torr of water vapor for about 24 hours results in the growth of a layer of SiO$_2$. This SiO$_2$ layer, which cannot be removed without damaging the Mo/Si multilayer structure, caused reflectivity to be reduced from 66% to 59%, a result that is unacceptable for operational

20   purposes.

Accordingly, what is required is a process for eliminating or significantly mitigating contamination and/or degradation of surfaces, and particularly surfaces of critical lithographic components, exposed to radiation in the presence of common contaminants such as hydrocarbons and water vapor. This

25   is especially true for the emerging lithographic processes that use shorter wavelength and thus higher energy radiation because of the significant potential for degrading critical components and the extreme sensitivity of these

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components to small changes in surface properties.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a process for mitigating or eliminating contamination of surfaces by common, adventitious atmospheric

5   molecular compounds dissociated by exposure to a radiative flux.

It is a further object to provide a process that operates effectively at sub-atmospheric pressures.

In the inventive process disclosed herein a gas or a mixture of gases is introduced into the environment of a surface(s) to be protected. The choice of

10   the gaseous species to be introduced is dependent upon the contamination as well as the ability of the gaseous species to bind to the surface to be protected. The latter criterion is invoked so that secondary electrons emitted from the surface in response to incident radiation can dissociate the adsorbed species. When the surface and associated bound species are exposed to radiation,

15   reactive species are formed that react with surface contaminants such as carbon or oxide films to form volatile products (e.g., CO, CO_2) which desorb from the surface.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates schematically a process resulting in surface

20   contamination.

Figure 2 illustrates schematically an embodiment of the present invention.

Figure 3A depicts the oxidation of a Si surface exposed to electron beam irradiation and water vapor.

25   Figure 3B shows mitigation of oxidation caused by the addition of ethanol.

Figure 4 shows the effect of water vapor and ethanol on a Si surface exposed to EUV radiation.

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Figure 5 shows the effect of molecular oxygen on carbon deposition.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a process for mitigating or eliminating contamination and/or degradation of surfaces having common, adventitious atmospheric contaminants adsorbed thereon and exposed to energetic radiation. These contaminants can include such species as hydrocarbons and water vapor that can be inherently present in the atmosphere of any system and generally can arise from such sources as materials of construction, vacuum pump oils and greases. Energetic radiation can be photons, electrons, or ions. This invention finds particular utility in those lithographic processes that employ highly energetic radiation such as extreme ultravoilet radiation and thus present a significant potential for contamination and, as a consequence, degradation of the performance of critical components.

While the process of the present invention is illustrated by application to extreme ultraviolet (EUV) lithography, and particularly to the mitigation of two common forms of contamination prevalent therein, carbon deposition and oxidation, its use is not limited to lithographic operations or elimination of carbon deposition or oxidation but is contemplated to be applicable generally.

The process of the present invention is illustrated and explained by reference to Fig. 2, which shows a Si surface 210 of a Mo/Si multilayer mirror. Generally, water vapor will be present in any system, particularly an unbaked vacuum system. Thus, adventitious water vapor arises from outgassing of various system components and these water vapor molecules can be adsorbed onto any surface, such as illustrated by Fig. 2. Subjecting surface 210 to high energy radiation, such as by EUV radiation, can cause secondary electrons to be ejected from surface 210. As discussed above, these electrons can react with the adsorbed water molecules causing them to dissociate into reactive oxygen species that will, in turn, react with the Si surface. Prior to exposing surface

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210 to incident radiation a small amount of a hydrocarbon gas that will also bind to surface 210 is admitted to the system. In the example illustrated by Fig. 2, the hydrocarbon gas is ethanol (C_2H_5OH). As was the case with bound water vapor, C_2H_5OH molecules bound to surface 210 will also be dissociated by the secondary electrons ejected from that surface. Reactive carbon fragments from the dissociated C_2H_5OH can react with reactive oxygen species on surface 210 to form volatile products such as CO and CO_2. In this way reactive oxygen species that could oxidize the Si surface and degrade its reflectivity are eliminated.

It will be appreciated that the process described above can function in the opposite manner. That is, when an environment is rich in carbon containing gases carbon contamination of surfaces can be produced by radiation exposure and the primary surface contaminant can be graphitic carbon. As discussed above, the presence of graphitic carbon on mirror surfaces can cause drastic reductions in their reflectivity for EUV radiation. Therefore, in these cases it is advantageous to admit an oxygen containing gas into the environment, such as water vapor or molecular oxygen. By substituting water vapor or molecular oxygen for a hydrocarbon gas, the same process as discussed above and illustrated in Fig. 2 can remove carbon contamination as carbon oxides (CO and CO_2).

A demonstration of the ability of the novel process described herein to eliminate surface contamination caused by exposure of adventitious molecular species to high energy radiation is given by the following examples.

EXAMPLE 1

Initially, a Si-terminated multilayer mirror was exposed to an electron beam current density of about 5 $\mu A/mm^2$ at a beam energy of 2 keV in the presence of about 2×10^{-7} Torr of water vapor. The chemical composition of the

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surface of the mirror was monitored as a function of time. The Auger peak

heights (which reflect the surface composition) of Si and SiO_2 are shown in Fig.

3A. It can be seen that the composition of the surface changed rapidly from Si

to SiO_2 as oxidation progressed with a corresponding degradation in

5   reflectivity.

The experiment above was repeated except that about 4×10^{-7} Torr of

ethanol was added to the 2×10^{-7} Torr of water vapor the environment contained.

As before, the chemical composition of the surface of the mirror was monitored

as a function of time and the results are shown in Fig. 3B. It can be seen that,

10 in contrast to the case where only water vapor was present, there is only a very

small amount of SiO_2 present on the Si mirror surface; an amount consistent

with the native oxide film typically found on Si. Further, post exposure

analysis of the surface of the exposed mirror surface showed the presence of a

film of graphitic carbon about 5 Å thick.

15 It is the presence of a native oxide film on Si that determines the choice

of the gas phase molecules used to protect against surface contamination.

Recalling that one important prerequisite for the choice of gas phase molecules

is that these molecules must first bind to the surface to be protected so that

dissociation by secondary electron emission can take place, thereby liberating

20 reactive species on the surface itself. Consequently, the preferred hydrocarbon

molecules are those that will bind to native surface constituents, for example, a

polar, hydroxylated film such as can be found on the surfaces of glasses,

metals, and silicon. Therefore, hydrocarbon molecules containing such polar

functional groups as ketones, aldehydes, esters, alcohols, amines, thiols, and

25 carboxylic acids that will bind well to hydroxylated surfaces are preferred. It

has been shown that non-hydrogen bonding hydrogen molecules, such as ethane,

cannot confer any protection from oxidation to Si surfaces, presumably because

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these non-polar molecules cannot bind to the Si surface, and by analogy to any hydroxylated surface. Moreover, because the sticking coefficients for both ethanol and water vapor on a graphitic carbon surface are very small the growth of the graphitic carbon film produced when ethanol was used to provide

5 oxidation protection tends to be self-limiting to a thickness of about 5 Å. Thus, the use of ethanol cannot lead to the formation of a catastrophically thick carbon layer, which itself would be undesirable. The self-limiting behavior leads to a large process latitude for the prevention method.

EXAMPLE 2

10 A Si-terminated Mo/Si mirror was exposed to 13.4 nm EUV radiation at a power level of about 7 mW/mm^2. The mirror was exposed to four different exposure conditions and the secondary electron emission was plotted as a function of time in Fig. 4. The exposure conditions were: background pressure (about 4×10^{-9} Torr); ethanol alone at a pressure of 4×10^{-7} Torr; water vapor

15 alone at a pressure of 2×10^{-7} Torr; and a mixture of ethanol (4×10^{-7} Torr) and water vapor (2×10^{-7} Torr). Secondary electron emission has been shown to be a useful monitor of the surface processes because the onset of oxidation is signaled by a very rapid increase in secondary electron emission that is due to EUV absorption by oxygen with subsequent emission of secondary electrons.

20 On the other hand, carbon deposition is signaled by a decrease in secondary electron emission due to the poor secondary electron emission characteristics of carbon.

Referring now to Fig. 4, it can be seen that exposure of the Si surface to water vapor in the presence of EUV radiation is accompanied by a rapid

25 increase in the secondary electron signal denoting the formation of an oxide film. However, when ethanol is admitted the increase in secondary electron

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signal attributable to surface oxidation is significantly reduced demonstrating
that the introduced hydrocarbon (ethanol) limited oxidation of the terminal Si
surface. Further adjustment in the water/hydrocarbon ratio could achieve a
balance point where carbon deposition and oxidation would balance each other.

5   As discussed above, exposure of carbon containing gases to high energy
radiation can result in the formation of graphitic carbon films on surfaces, such
as mirror surfaces, with detrimental effects to their reflectivity for EUV
radiation. However, by the use of water vapor or oxygen in the disclosed
process it is possible to remove graphitic carbon films. This is demonstrated in
10   the example below.

EXAMPLE 3

Referring now to Fig. 5, where it is shown that electron irradiation of
adventitious hydrocarbon molecules present in a vacuum system can result in
carbon deposition. Here, a 2kV electron beam, at a current density of about
15   $5\mu A/mm^2$, is incident onto a Si-terminated Mo/Si multilayer mirror. The mirror
is maintained at a vacuum of about 5×10^{-10} Torr. As exposure to the incident
electron beam increases, an increase in atomic percentage of carbon on the
mirror surface takes place. After about 120 minutes of exposure, about 2×10^{-8}
Torr of molecular oxygen is admitted to the vacuum chamber. At that time, the
20   increase in carbon deposition stops and no measurable additional carbon
deposition occurs

Those skilled in the art will appreciate the importance of not adversely
impacting the transmission of radiation, particularly for lithographic
applications, by added gaseous components. The present invention provides an
25   important advantage in this regard since, as exemplified above, the partial

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pressures of the various added gaseous molecular species need be only as high as necessary to affect surface chemistry. The use of gas pressures up to about 1×10^{-5} Torr would generally be adequate to provide a protective effect for most contamination problems while having negligible impact on lithographic

5 throughput or uniformity. By way of example, the transmission of EUV radiation at 13.4 nm through 2 meters of a water/ethanol gas mixture, with each component at a partial pressure of about 1×10^{-5} Torr would be reduced by only about 0.05%.

In summary, the present invention provides a process for reducing or

10 eliminating contamination and oxidation of surfaces caused by the interaction of high energy radiation on adventitious impurities. In particular, the process disclosed here can be used for reducing or eliminating oxide or carbon films on surfaces, such as the surface of silicon mirrors. Most particularly, the present invention provides special advantage in removing or reducing surface

15 contamination in those components, such as masks and imaging optics, used in lithographic applications.

The above described method and the examples pertaining thereto are merely illustrative of applications of the principles of this invention and many other embodiments and modifications can be made by those of skill in the art

20 without departing from the spirit and scope of the invention as defined in the claims.

CLAIMS

What is claimed:

1. A process for eliminating contamination of surfaces exposed to radiation,

5   comprising:

a) providing an enclosed space having a surface disposed therein, wherein

the atmosphere within the enclosed space contains contaminants;

b) introducing a gas capable of binding to the surface and reacting with

the atmospheric contaminants into the enclosed space; and

10   c) subjecting the contents of the enclosed space to extreme ultraviolet

radiation.

2. The process of claim 1, wherein the gas is comprised of hydrocarbon

molecules.

3. The process of claim 2, wherein the hydrocarbon molecules contain at least

15   one functionality selected from the group that includes ketones, aldehydes,

esters, alcohols, amines, thiols, and carboxylic acids.

4. The process of claim 3, wherein the gas comprises ethanol.

5. The process of claim 1, wherein the gas is water vapor or oxygen.

6. The process of any preceding claim, wherein the gas comprises a mixture of

20   gases.

7. The process of claim 6, wherein the mixture of gases is selected from the

group including a hydrocarbon gas, water vapor, and oxygen.

8. A process for eliminating contamination of lithographic surfaces,

comprising:

25   a) providing an enclosed space having at least one surface disposed

therein and wherein the enclosed space is at sub-atmospheric pressure and the

atmosphere within the enclosed space contains contaminants;

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b) introducing a gas capable of binding to the surface and reacting with the atmospheric contaminants into the enclosed space; and

c) subjecting the contents of the enclosed space to extreme ultraviolet radiation.

5   9. The process of claim 8, wherein the gas is comprised of hydrocarbon molecules.

10. The process of claim 9, wherein the hydrocarbon molecules contain at least one functionality selected from the group that includes ketones, aldehydes, esters, alcohols, amines, thiols, and carboxylic acids.

10   11. The process of claim 10, wherein the gas comprises ethanol.

12. The process of claim 8, wherein the gas is water vapor or oxygen.

13. The process of any preceding claim, wherein the gas comprises a mixture of gases.

14. The process of claim 13, wherein the mixture of gases is selected from the

15   group including a hydrocarbon gas, water vapor, and oxygen.

15. The process of claim 8, wherein the partial pressure of the gas is less than about 10^{-5} Torr.
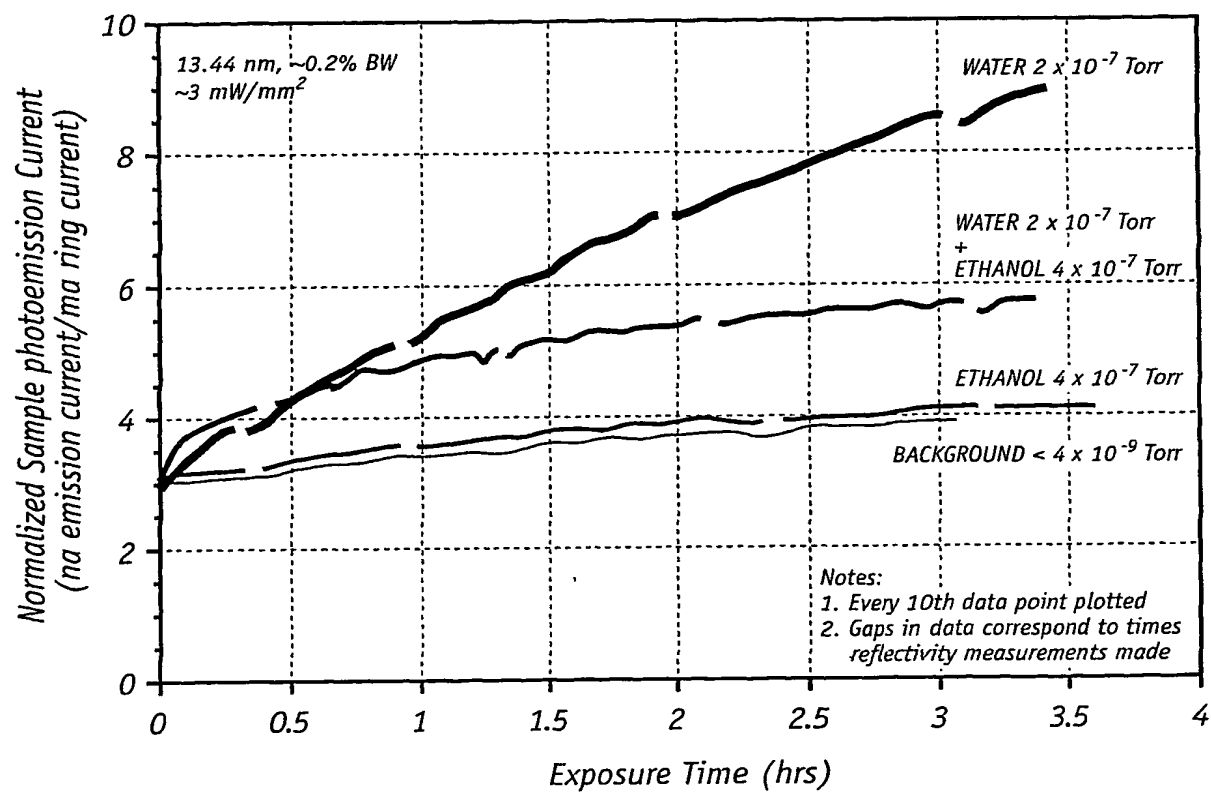
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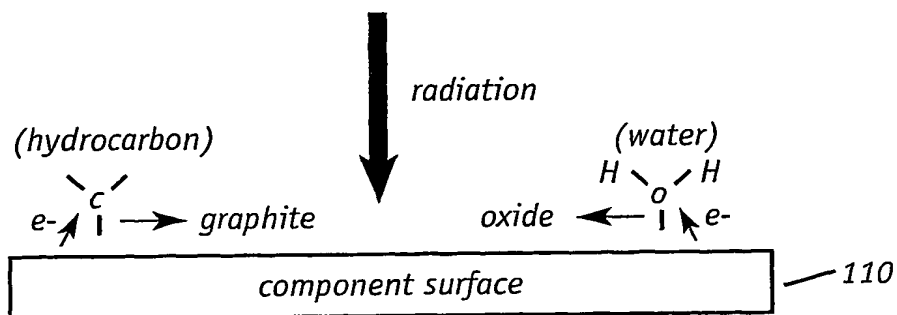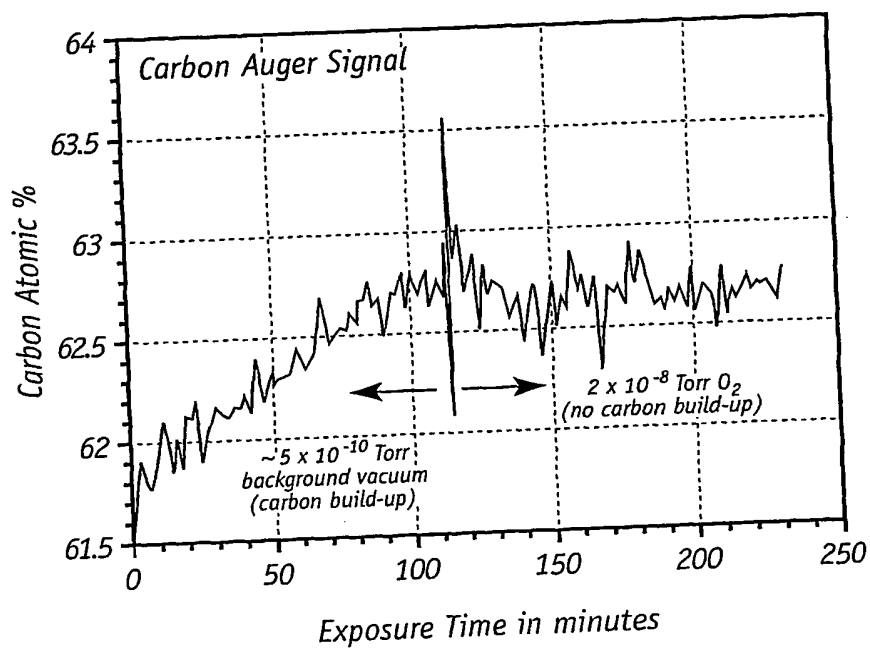

FIG. 1
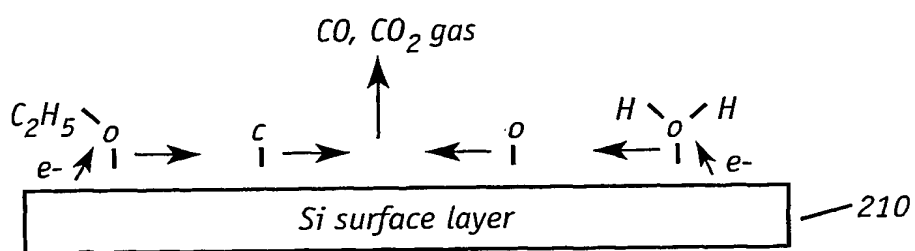
FIG. 2

2 x 10-7 Torr Water
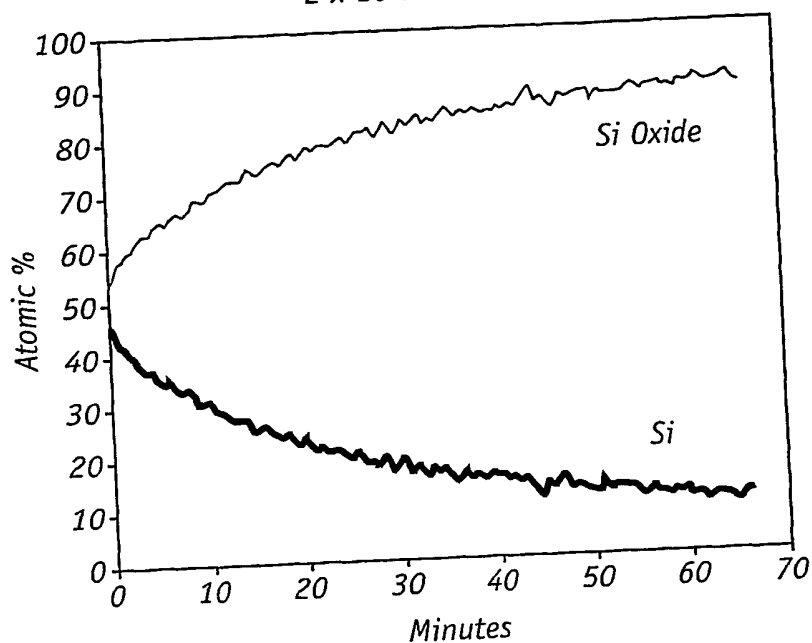
FIG. 3A

2 x 10-7 Torr Water, 4 x 10-7 Torr EtOH
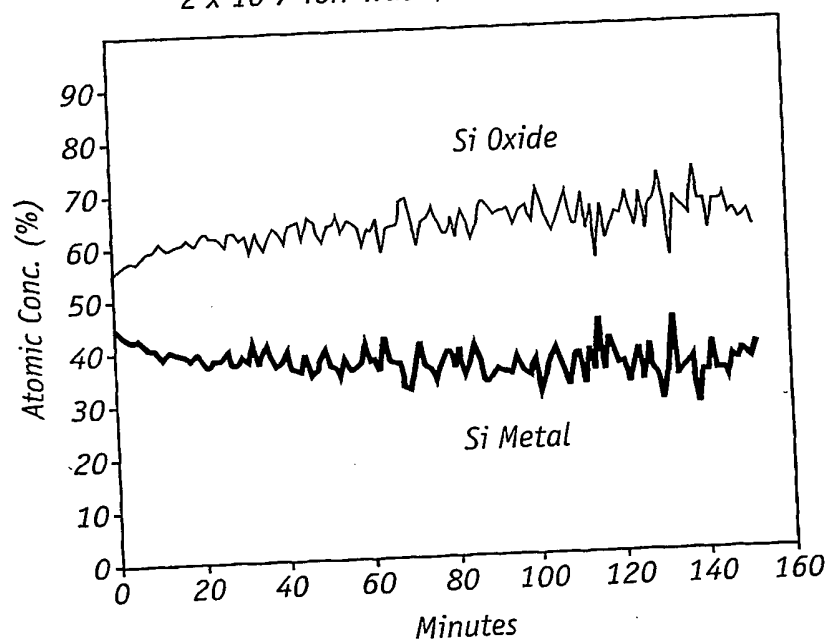
FIG. 3B

FIG. 4

FIG. 5

I.   tional Application No

PCT/US 00/35394

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   G03F7/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7   G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, INSPEC, WPI Data, IBM-TDB, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PRUETT C H: "Care and conditioning of optical surfaces for SRS beamlines" VACUUM DESIGN OF ADVANCED AND COMPACT SYNCHROTRON LIGHT SOURCES, UPTON, NY, USA, MAY 1988, no. 171, pages 167-174, XP008000138 AIP Conference Proceedings, 1988, USA ISSN: 0094-243X page 171 -page 173	1,5-8, 12-15
E	US 6 252 648 B1 (HASE TOMOHARU ET AL) 26 June 2001 (2001-06-26) & JP-A-11224839 (published 17-08-1999) column 3, line 45 - line 53 column 5, line 4 - line 5	1,5-8, 12-15
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[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

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Date of the actual completion of the international search

31 January 2002

Date of mailing of the international search report

19/02/2002

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category°	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	KUNZ R R ET AL: "Experimentation and modeling of organic photocontamination on lithographic optics" JOURNAL OF VACUUM SCIENCE & TECHNOLOGY B (MICROELECTRONICS AND NANOMETER STRUCTURES), MAY 2000, AIP FOR AMERICAN VACUUM SOC, USA, vol. 18, no. 3, pages 1306-1313, XP002188756 ISSN: 0734-211X	

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US 6252648	B1	26-06-2001	JP	11224839 A	17-08-1999
			US	2001028447 A1	11-10-2001